ST ALOYSIUS
(DEEMED TO BE UNIVERSITY)
MANGALURU 575003 - INDIA
ESTD : 1880

Syllabus for PhD Entrance Exam
January -2025

Department: CHEMISTRY

PART I – RESEARCH METHODOLOGY

Unit 1 **Research:** Definition, characteristics, objectives, scientific research, need and importance of research. Types of Research, significance of research in chemical sciences, Research Strategies - meaning and types.

Unit 2 **Research Problem –** Identification and meaning, selecting and formulation of a problem, Research objectives- research design, hypothesis, significance and report writing.

Unit 3 **Review of Literature** – meaning and need for literature review, sources of literature review, reporting the review of literature, identification of research gap. Print Sources of information – Primary, Secondary, Tertiary sources.

Unit 4 **Scientific Writing:** Scientific document, Organization and writing of research paper, short communications, review articles, monographs, technical and survey reports, authored books, edited books and dissertation.

Unit 5 **Research Ethics and Intellectual Property Rights (IPR):** Ethics – meaning and definition, Ethical issues, ethical committees. Rights and obligations of Research Participants. Scientific misconduct – falsification, fabrication and plagiarism. Publication ethics – meaning and importance, plagiarism and Self-plagiarism. Intellectual property rights and patent laws.

References:

1. Kothari C R., Research methodology: Research & Techniques, New Age International Publishers, New Delhi.
2. A K Singh, Tests, Measurements and Research Methods in Behavioral Sciences, Bharathi Bhawan (Publishers & Distributors), New Delhi.
3. David I Bainbridge (2012), Intellectual Property Rights, Long man Publication.
4. Y. K Singh., Fundamentals of Research Methodology and Statistics, New International (P) Ltd., New Delhi.

Part II – Domain Specific

Unit 1 **Acids and Bases:** Factors affecting strengths of hydracids, oxoacids and Lewis acids and bases, Hard & soft acid-bases, Lux-Flood, Usanovich & solvent system definition of acids and bases, solvent levelling effect, HSAB concepts, Symbiosis. Super acids - Hammet acidity function,

Unit 2 **Coordination Chemistry:** Coordination numbers 2-10 and their geometry, Crystal Field Theory- Salient features, dorbital splitting in octahedral, tetrahedral, square planar and tetragonal complexes, spectrochemical series, Jahn-Teller distortions.

Stability of Metal Complexes - Stepwise and overall formation constants, factors affecting stability of metal complexes, determination of stability constants of metal complexes by spectrophotometry (Job's method)

Unit 3 **Stereochemistry;** Chiral centres, chirality, Chiral molecules, **Optical Isomerism:** Conformation and configuration of molecules, (R,S) system of nomenclature, threo and erythro isomers, methods of resolution, stereo specific and stereo selective synthesis, Optical activity in the absence of chiral carbon-biphenyls, allenes and spiranes. Stereochemistry of compounds containing nitrogen, sulphur and phosphorus. Conformational analysis of cycloalkanes and decalins.

Unit 4 **Organic Name Reactions**: Reactions and Mechanisms of the following: Stobbe condensation, Darzen condensation, Gattermann-Koch reaction, Cannizzaro reaction, Chichibabin reaction, Benzoin condensation, Claisen-Schmidt condensation, Simon-Smith reaction, Stork Enamine reactions, Hofmann-Loffler-Freytag reaction, Woodward and Prevost Hydroxylation, Bucherer reaction, Ullmann reaction. Wittig reaction-Mitsunobu reaction, Stephen reaction.

Unit 5 **Aliphatic Nucleophilic Substitution Reactions:** Mechanism of aliphatic nucleophilic substitution reactions - S_N1, S_N2 and S_Ni. Stereochemistry of nucleophilic substitution reactions. allylic, vinylic and benzylic nucleophilic substitution reactions, neighbouring group. Factors influencing the rates of nucleophilic substitution reactions.

Aliphatic Electrophilic Substitution Reactions: Bimolecular mechanisms - S_E1, S_E2 and S_Ei mechanism

Unit 6 **Chemical kinetics:** Complex reactions- parallel, consecutive and reversible reactions. Photochemical (hydrogen-halogen reactions- derivation of rate equation for H_2-Br_2) and oscillatory reactions. Substituent effects on the rates of reactions-Hammett and Taft equations, Collision and transition state theory of reaction rates, catalysis- homogenous, heterogenous and enzyme catalysis. Michaelis Menten equation.

Surface reaction kinetics: adsorption isotherms, Langmuir and Freundlich isotherm. Multilayer adsorption-BET equation-its derivation and application in surface area determination.

Unit 7 **Electrochemistry:** Nernst equation, Kohlrausch law of independent migration of ions. Activities in electrolytic solutions, mean activity coefficient Ionic atmosphere, Debye – Huckel - Onsager equation of conductivity and its validity. Galvanic cells. Reference electrodes, Calomel, Quinhydrone, Ag-AgCl and glass electrode.

Unit 8 **Chromatography -** Introduction; classification - types of chromatography, partition and adsorption, Rf value. Principle and Applications of Thin layer, paper and column chromatography, Gas chromatography, HPLC and Ion exchange chromatography.

Thermal Methods of Analysis: Principle and applications of TGA, DTA and DSC.

Optical Methods of analysis: Principle and applications of AAS, AES and spectrofluorimetry.

Unit 9 **Microwave Spectroscopy:** rotation spectra of diatomic and polyatomic molecules. Rigid and non-rigid rotator models. Derivation of the expression for moment of inertia of diatomic molecule, isotope effect on rotation spectra. Moment of inertia expression for linear polyatomic molecules.

Vibrational Spectroscopy: Vibration spectra of diatomic molecules - linear harmonic oscillator, vibrational energies, zero point energy, force constants and bond strengths, energy curves for simple harmonic oscillator. Anharmonicity of molecular vibrations - Morse potential energy diagram, fundamental, overtones and hot bands.

Unit 10 **UV absorption spectroscopy:** Beer-Lambert law, Molar absorptivity, theory of electronic spectra, formation of bands, effect of conjugation with examples; Concept and effect of addition of chromophore and auxochrome. Absorption and intensity shifts- Bathochromic, hypsochromic, hyperchromic and hypochromic shifts.

NMR AND MASS SPECTROMETRY:

Shielding and deshielding in NMR, Nuclear magnetic resonance (^{1}H and ^{13}C) Spectroscopy- Chemical shift, factors affecting chemical shift values.

Mass Spectrometry: Basic principles, ionization technique MALDI, molecular ions, meta-stable ions and isotope ions. Fragmentation processes-representation of fragmentation, basic fragmentation types and rules. McLafferty rearrangement.

References:

1. Puri, Sharma and Kalia (2016), Principles of Inorganic chemistry, Vishal Publishing House, 33rdEdition.
2. J. D. Lee (2014), Concise Inorganic Chemistry, Blackwell Science, 5th Edition
3. K. J. Laidler (2003), Chemical Kinetics, Harper and Row, 3rd Edition.
4. S. Glasstone (2006), Electrochemistry, Affiliated to East-west press, 1st Edition.
5. Bockris and Reddy (1998), Modern electrochemistry - vol I 2A &2B, Plenum, New York, 2nd Edition
6. Gurudeep R. Chatwal, (2010), Instrumental methods of Chemical Analysis, S Chand.
7. R. A. Day and A. L. Underwood (2008), Quantitative Analysis, Prentice-Hall, 6th Edition
8. A. Bahl and B. S. Bahl (2019), A Textbook of Organic Chemistry, S. Chand Publications, 22nd Edition.
9. P. Y. Bruice (2018), Organic Chemistry, 3rd Edition
10. V. K. AhIuwalia and K. Parashar (2006), Organic Reaction Mechanisms, Narosa Publishers, 3rd Edition.
11. Banwell & McCash (2015), Fundamentals of Molecular Spectroscopy, Tata McGraw Hill, 5th Edition.
12. Y. R. Sharma (2013), Elementary organic spectroscopy, S. Chand, 5th Edition.